REMARKS

Applicants hereby amend claim 13. Accordingly, claims 13-20 remain pending in the application.

35 U.S.C. § 102 and 103

The Office Action rejects claims 13-18 under 35 U.S.C. § 102 over Yoon et al., 83 J.Appl. Phys. 7 (1998) ("Yoon"); claims 19-20 under 35 U.S.C. § 103 over Yoon in view of Hsu et al. U.S. Patent 6,048,738 ("Hsu"); claims 15-17 under 35 U.S.C. § 102 over Suzuki et al., 36 Jpn. J. Appl. Phys. 9B (1997) ("Suzuki"); and claims 18-20 under 35 U.S.C. § 103 over Suzuki in view of Hsu.

REJECTIONS BASED ON YOON

Yoon was published on 1 April 1998. The Korean patent application from which this application claims priority was filed on 31 December 1997. Applicants submit attached herewith a certified English translation of the Korean priority document, thereby establishing an invention date for the present application which predates the publication of Yoon.

Therefore, as indicated on page 2 of the Office Action, Applicants respectfully submit that the Yoon reference has been overcome and respectfully request that the rejection of claims 13-18 over Yoon and claims 19-20 over Yoon and Hsu be withdrawn.

Accordingly, claims 13-14 having only been rejected based on Yoon, Applicants respectfully submit that claims 13-14 are now in condition for allowance.

REJECTIONS BASED ON SUZUKI

Claims 15-17

Claims 15-17 depend from claim 13. Accordingly, among other things, the methods of claims 15-17 each include a feature of forming a ferroelectric layer on the

lower seed layer by one of a sputtering or a CVD process.

Meanwhile, <u>Suzuki</u> is specifically directed toward a method of low temperature processing of a PZT thin film without annealing in a special atmosphere (e.g., a vacuum). Toward this end, <u>Suzuki</u> discloses a method of repeatedly **dip-coating** very thin (40-60 nm thick) PT and PZT layers onto a silica glass substrate with a Pt electrode. <u>Suzuki</u> repeatedly disparages the single-seeding process.

<u>Suzuki</u> does not disclose or suggest forming a ferroelectric layer on the lower seed layer by one of a sputtering or a CVD process, and indeed, teaches away from the methods of claims 15-17.

Furthermore, all of the methods of claims 15-17 include forming an upper electrode on the upper seed layer. The Office Action states that <u>Suzuki</u> discloses in section 3.2 measuring permittivity "which includes formation of an electrode on the PbTiO3 layer." Applicants respectfully disagree. Applicants do not see any mention of an upper electrode in <u>Suzuki</u>, including particularly in section 3.2. As best as Applicants can understand the Office Action, it appears to be the Examiner's position that the fact that <u>Suzuki</u> discloses measuring permittivity of the thin PZT film somehow *inherently* discloses forming an upper electrode on the upper seed layer. Applicants respectfully disagree. It appears that <u>Suzuki</u> is silent as to how the permittivities of FIG. 5 were obtained. However, Applicants respectfully submit that the permittivities of thin PZT films are commonly measured using a swept frequency permeameter without any upper capacitor electrodes formed on the upper layer, as discussed, for example, in the attached paper, "High Frequency, Transient Magnetic Susceptibility of Ferroelectrics," 80 J. Appl. Phys. 8 (Oct. 15, 1996) (<u>see</u> FIG. 3). Accordingly, Applicants respectfully submit that <u>Suzuki</u> fails to disclose forming an upper electrode on the upper seed layer, and accordingly cannot satisfy the requirements for a rejection of claims 15-17 under 35 U.S.C. § 102.

Therefore, for at least the foregoing reasons, Applicants respectfully submit that claims 15-17 are patentable over <u>Suzuki</u>.

Claims 18-20

The Office Action cites <u>Hsu</u> solely for the switching element, the source/drain regions, and steps for forming the upper and lower electrodes noted as missing in <u>Suzuki</u>. However, Applicants respectfully submit that <u>Hsu</u> fails to cure the other defects in <u>Suzuki</u> discussed above with respect to claims 15-17. Accordingly, it is respectfully submitted that claims 18-20 are patentable over any combination of <u>Suzuki</u> and <u>Hsu</u>.

CONCLUSION

In view of the foregoing explanations, Applicants respectfully request that the Examiner reconsider and reexamine the present application, allow claims 13-20, and pass the application to issue. In the event that there are any outstanding matters remaining in the present application, the Examiner is invited to contact Kenneth D. Springer (Reg. No. 39,843) at (703) 715-0870 to discuss these matters.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies to charge payment or credit any overpayment to Deposit Account No. 50-0238 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17, particularly extension of time fees.

Respectfully submitted,

VOLENTINE FRANCOS & WHITT, P.L.L.C.

Date: 12 October 2004   By: _____

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High-frequency, transient magnetic susceptibility of ferroelectrics

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A significant high-frequency magnetic susceptibility was measured both in weakly polarized and nonpolarized samples of barium titanate, lead zirconate titanate, and carnauba wax. Magnetic susceptibility measurements were made from 10 to 500 MHz using a thin film permeameter at room temperature; initial susceptibilities ranged from 0.1 to 2.5. These values are larger than expected for paramagnets and smaller than expected for ferromagnets. It was found that the magnetic susceptibility decreases rapidly with exposure to the exciting field. The origin of the magnetic susceptibility is thought to originate with the applied time varying electric field associated with the susceptibility measurements. An electric field acts to rotate an electric dipole, creating a magnetic quadrupole if the two moments are balanced, and a net magnetic dipole moment if imbalanced. It is thought that local electrostatic fields created at ferroelectric domain discontinuities associated with grain boundaries create an imbalance in the anion rotation that results in a net, measurable, magnetic moment. The origin of the magnetic aftereffect may be due to the local heating of the material through the moving charges associated with the magnetic moment. © *1996 American Institute of Physics.* [S0021-8979(96)07920-0]

INTRODUCTION

This work is motivated by the results of an extended effective medium model that accurately describes the measured frequency dependent complex permittivity spectra of ferroelectrics.[1,2] To briefly summarize the key points of the model, field coefficients determined by an exact electromagnetic solution of scattering of a plane wave from a sphere are combined with the Clausius–Mossotti equation to obtain expressions for the effective electromagnetic properties of a material consisting either of an amorphous or polycrystalline arrangement of spherical grains that have arbitrary scalar values of complex permeability $\mu = \mu' - j\mu''$ and complex permittivity $\epsilon = \epsilon' - j\epsilon''$. The product of the incident wave vector (k) and sphere radius (a) is less than one and the product of the internal wave vector (k_i) and sphere radius, $k_i a = ka\sqrt{\mu\epsilon}$, is unconstrained; note that $k = 2\pi/\lambda$. As it relates to the experimental work described in this article, Fig. 1 is the measured frequency dependent capacitance in pF, which is directly proportional to ϵ', of $BaTiO_3$ by von Hipple.[3] Figure 2 is a plot of ϵ' calculated using the effective medium theory described in Refs. 1 and 2 with the grains, or spheres, assigned a frequency dependent ϵ determined by a coherent rotation model,[4] and a small, frequency dependent grain permeability also determined using a coherent rotation model.[2,5] The model accurately predicts the measured permittivity spectrum of $BaTiO_3$ (Ref. 3) and $Sn_2P_2S_6$ (Ref. 6) if it is postulated that a small, time varying magnetic field acts upon the granular interfaces. The success of the model, and the development of a sensitive radio-frequency magnetic susceptibility measurement device[7] led to an investigation of whether ferroelectrics do have measurable frequency dependent permeabilities that have previously been undetected.

The magnetic susceptibility spectra of unpolarized barium titanate $BaTiO_3$, lead zirconate titanate $PbTi_{45}Zr_{55}O_3$ (PZT), and carnauba wax samples were measured using a thin film high frequency permeameter that has a low level susceptibility detection limit of approximately 3 nm^2 over the frequency range of interest,[7] about 100 more times sensitive than a stripline cavity.[8] The pickup coil detects magnetic flux proportional to the relative magnetic susceptibility of the sample, a dimensionless quantity, and the cross sectional area of the sample perpendicular to the detecting coil and therefore has units of area; if the thickness of the film is known the magnetic susceptibility can be uniquely determined. It is found that approximately 20 of the 100 samples measured demonstrated a frequency dependent magnetic susceptibility that disappeared after approximately 1 min in the permeameter. It was found that the magnetic susceptibility could be returned to the sample by placing it between a (nonsaturating) ac or dc 200 V/cm electrical grid, oriented parallel or perpendicular to the basal plane of the sample; the renewed magnetic susceptibility values were much smaller than the initial measurement and after the sample had gone through, at most, three such renewal iterations no magnetic susceptibility was detected. A suggested origin of the magnetic susceptibility and its aftereffect are described.

EXPERIMENT

The susceptibility measurements were made with a swept frequency permeameter,[7] a schematic drawing of which is shown in Fig. 3. Designed for thin film samples, the physical property measured is the product of the relative magnetic susceptibility χ, a unitless quantity, and sample cross sectional area. Generally speaking, the permeameter is a shorted, rectangular coaxial transmission line. Identical pickup loops are placed between the rectangular plates and oriented so the magnetic driving field induces equal loop
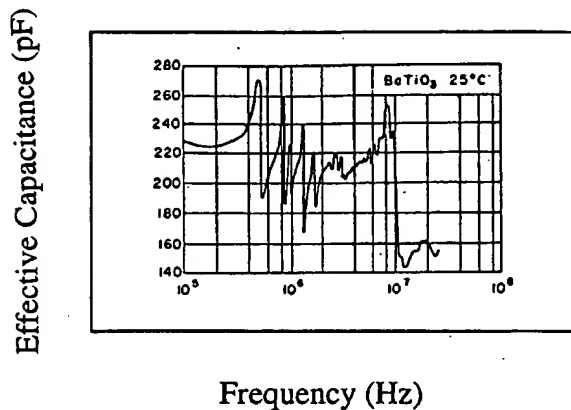

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FIG. 1. Resonance spectrum of a BaTiO₃ disk (after Ref. 3).

FIG. 2. ϵ_{eff} calculated using effective medium theory (Refs. 1 and 2) and parameters of Ref. 11 to describe BaTiO₃; a frequency dependent, complex relative magnetic susceptibility of approximately 20 is assumed.

voltages. A magnetic test sample placed within one of the loops induces an additional voltage, via additional lines of flux, which is measured as a difference signal; there is no contact between the test sample and pickup loop. A microwave scattering parameter test set, controlled by a network analyzer, is used to measure the scattering parameters of the jig. The small signal, high frequency susceptibility is determined from the scattering parameters. As can be seen from Fig. 3, the electric field is perpendicular to the basal plane of the sample, whereas the magnetic field is parallel. The strength of the magnetic driving field in the permeameter was approximately 0.05 A/m; the strength of the electric driving field was approximately 0.9 V/cm.

We measured disks of BaTiO₃ 9.3 mm in diameter×1.2 mm thick, solution cast thin films of PZT, 2.5 cm×2.5 cm×25 μm, and carnauba wax electrets 2.5 cm×2.5 cm ×1.5 mm. The electrets were made by pouring melted carnauba wax into a mold while it was subjected to a 200 V/cm dc polarizing field. A Corning microcover glass slide was used as a substrate for the carnauba wax electrets; the BaTiO₃ and PZT samples were self-supporting. The magnitude of the magnetic aftereffect was determined by repeatedly measuring an undisturbed sample placed within the permeameter; each measurement took approximately 16 s. In all cases the magnitude of the susceptibility spectra dropped rapidly between measurements, demonstrating a magnetic aftereffect. The ratio of the second to first measurement was typically about 0.1; the maximum about 0.5. Each sample was repeatedly measured until the ratioed signal fell into the noise, which typically occurred with the third measurement or after the sample had been inside the jig for a time greater than 48 s.

After the measured susceptibility had fallen into the noise, each sample was removed from the jig and placed in either an ac or dc polarizing field of approximately 200 V/cm, with the polarizing field both in and out of the basal plane of the samples, and then remeasured. The sample would typically regain its positive magnetic susceptibility, which again decreased with time under measurement until the signal fell into the noise. After several such iterations,
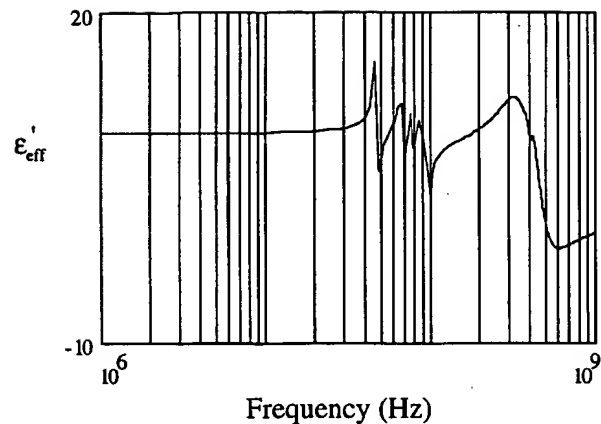
usually two or three but as many as five, the magnetic response ceased entirely and could not be renewed in the sample. There was no discernible dependence on how the sample was oriented within the polarizing field. All work was done at room temperature.

Although measured magnetic susceptibilities were typically small, approximately 0.1–0.5, on several occasions values in the range of $\chi \approx 1.0$–2.5 were obtained. The time dependent aftereffect measurements showed that the measured susceptibility decreased by at least a factor of 2 during the measurement. Therefore the initial susceptibility of the samples could be in the tens.

Figure 4 shows the complex magnetic susceptibility spectrum of a self-supporting (no substrate) 25-μm-thick PZT film sample from 100 to 500 MHz. Figure 5 shows the relative magnitude of the magnetic aftereffect, or time-dependent decrease in measured magnetic susceptibility, for one measurement sequence over the frequency range of 100–500 MHz. A PZT sample was measured, the susceptibility spectra stored in a computer, the sample left undisturbed and immediately remeasured, and the ratio taken. There was a 50% reduction in measured susceptibility magnitude during the (approximately) 16 s duration it took to remeasure the sample; the next measurement reduced the value down to approximately 15%, the fourth measurement returned a null value. The negligible imaginary component of Fig. 5 indicates that the relative phase of the complex susceptibility stays fixed with time, although the magnitude is decreasing.

The measured range of magnetic susceptibilities for the PZT and BaTiO₃ samples was essentially the same, 0.1–2.5. The largest measured magnetic susceptibility value for a carnauba electret was 0.5. There was no discernible difference between PZT and BaTiO₃ in terms of the magnetic aftereffect, however the electret signal decreased approximately twice as fast as that of the ferroelectric ceramics. Before the electrets had dried to a hard paste, exposure to the polarizing
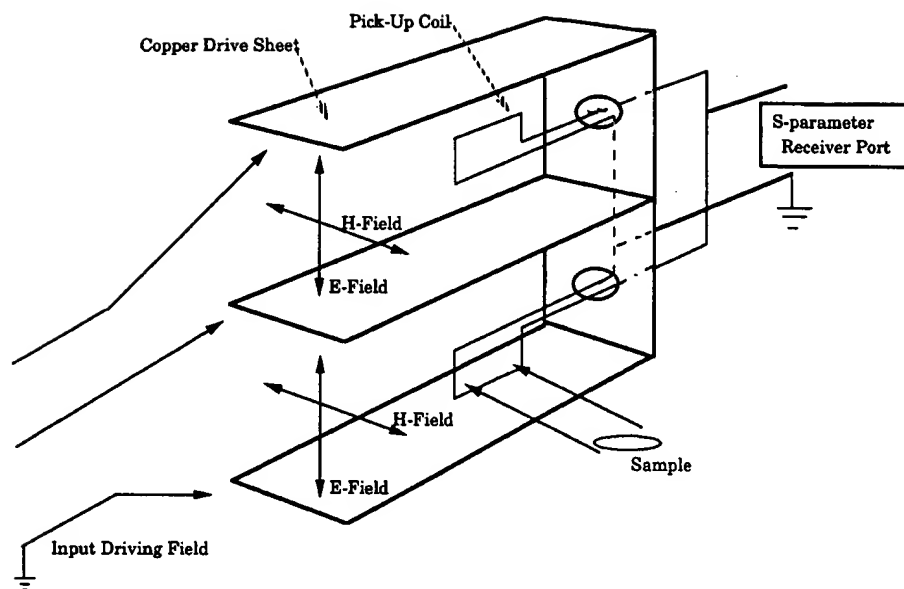
FIG. 3. Schematic drawing of permeameter (after Ref. 7) showing sample and field orientations.

field reintroduced the magnetic susceptibility; after hardening the polarizing field had no discernible effect.

THEORY AND DISCUSSION

What is the origin of this frequency dependent magnetic susceptibility? The ferroelectrics measured have no permanent magnetic moment, and so the measured magnetic susceptibility must be induced by either the magnetic or electric field. According to Lenz's law, the incident magnetic field causes free charges to rotate in a direction that opposes the incident magnetic field. Therefore if the magnetic suscepti-

bility had its origin in the incident rf magnetic field, it would be diamagnetic, or negative valued. Since the measured magnetic susceptibility is positive valued, the origin must lie with the electric field.

An electric field applied perpendicular to the axis of an electric dipole causes the dipole to rotate; in free space the rotation is such as to align the dipole moment with the applied electric field. An electric dipole has charges of opposite sign that, when rotating, produce oppositely directed mag-
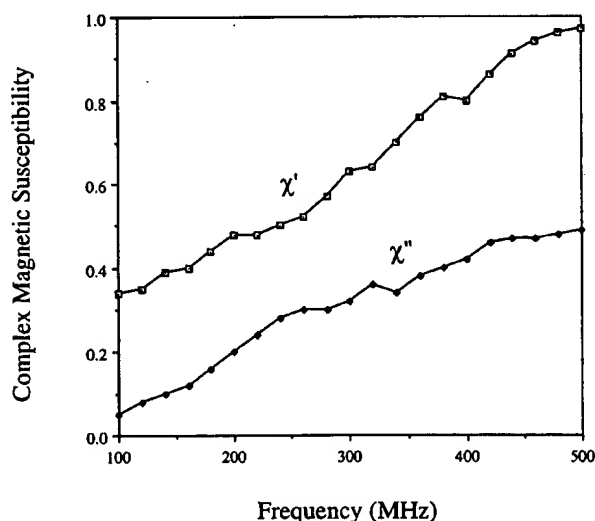

Frequency (MHz)

FIG. 4. Measured complex magnetic susceptibility spectrum of PZT (first measurement of the sample). Elapsed measurement time approximately 16 s.
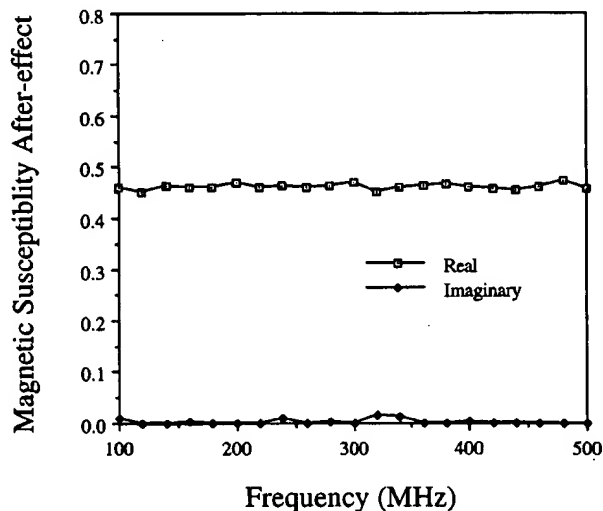

Frequency (MHz)

FIG. 5. Demonstration of time decrease of magnetic susceptibility of PZT. The measurements is the ratio of the magnetic susceptibility spectrum of the PZT sample exposed to measurement field 32 s to that of the same, undisturbed sample measured 16 s earlier; there has been an approximate 50% reduction in the measured magnetic susceptibility.
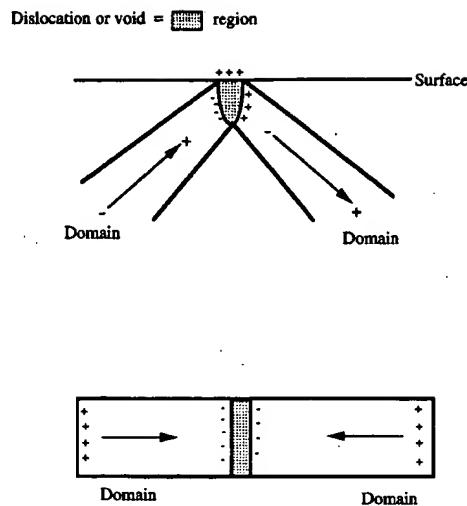
Dislocation or void = ▦ region

FIG. 6. Two illustrative domain configurations with locally intense electrostatic fields.
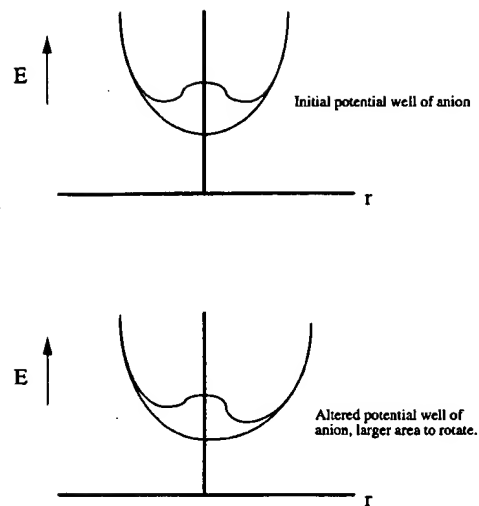

FIG. 7. (a) Schematic drawing of the potential well for an anion in the lattice. (b) Schematic drawing of the potential well for an anion perturbed by local electric field due to domain dislocation across the grain boundary or void.

netic dipole moments, i.e., a magnetic quadrupole. Due to the field symmetry of the magnetic quadrupole moment, it cannot be detected using a permeameter. However if one of the electric charges is constrained, the two halves of the induced magnetic quadrupole are unequal and there may be a net, measurable, magnetic dipole moment.

Inside a ferroelectric material the direction of an applied electric field is locally dependent upon the microstructure, and the plane of rotation is locally dependent upon the orientation of the electric dipole moment. Letting $\bar{a}$ represent a vector, let us consider a ferroelectric domain with electric dipole moment $\bar{p}$ submerged in a time varying plane wave with electric field intensity $E(t)$. The resulting torque on each dipolar cell is equal to

$$\bar{T} = \bar{p} \times \bar{E}(t). \tag{1}$$

This torque acts to rotate the dipole moments, or polarization. Referring to the permeameter geometry shown in Fig. 3, if the moments are oriented parallel to $E(t)$, there is no torque, and hence no charge rotation. If the moments are oriented in the plane of the sample, the charges rotate about $\bar{E}(t)$ generating a magnetic field perpendicular to the plane of the pickup coil of the permeameter, which is therefore undetected.

In ferroelectrics, very intense, structure-dependent local fields can be developed within the material, particularly across grain boundaries with discontinuities in the electric domains. Figure 6 is a schematic drawing of two examples of ferroelectric domain discontinuities that result in intense, local electric fields. Such intense local fields alter the potential well seen by an anion within a lattice. For example, Fig. 7(a) is a schematic drawing of the potential well seen by an anion within a lattice. Locally, an intense electrostatic field distorts the potential well, tipping it on its side, as illustrated in Fig. 7(b); this permits the anion to rotate more freely. The distortion of the potential well leads to an imbalance in the generated magnetic dipoles, per Eq. (1), and hence a net magnetic

susceptibility. Alternatively, it is known that the dielectric constant of $BaTiO_3$ (Ref. 9) and the relaxor ferroelectric material $Pb(Mg_{1/3}Nb_{2/3})O_3$ (Ref. 10) is smaller at the surface of the sample than the interior or bulk value; it is possible that the postulated local field discontinuities responsible for the magnetic dipole moment are associated with this transition or discontinuity in permittivity.

To obtain an expression for the induced magnetic susceptibility, let us consider anion rotation within a cell of width $2b$, the resultant magnetic moment is $\omega Q b^2/2$, where Q is the net charge, and ω is the radian frequency. Letting N represent the number of contributing anions per unit volume, the magnetic moment per unit volume is given by

$$M = \frac{\omega Q b^2}{2} N. \tag{2}$$

If Δb is the effective change in the radius of rotation due to a locally intense electrostatic field, the change in the magnetic moment per unit volume is given by

$$\Delta M \approx \omega Q b N \Delta b. \tag{3}$$

The incremental change in the rotation radius of the anion Δb is dependent upon the applied time dependent electric field $E(t)$, and a constant α that would depend upon the material and the degree to which the potential well is altered by local electrostatic fields. Thus

$$\Delta M \approx \omega Q b N \alpha E(t). \tag{4}$$

Since in an incident plane wave, $E(T) = \eta H(t)$, where η is the impedance of the material, the moment may now be written as a function of H

$$\Delta M \approx \omega Q b N \alpha \eta H(t). \tag{5}$$

The magnetic susceptibility χ, defined as M/H, can be determined from Eq. (5)

$$\chi = \omega Q b N \alpha \eta. \qquad (6)$$

Stripline cavity measurements of PZT showed the 200 MHz permittivity to be $\epsilon = 180 - j20$. It is possible to estimate the local dipole moment,[11] Q, b, and $\eta = 377/\sqrt{\epsilon}$, but neither N nor α since there appears to be no certain way of knowing either the volume fraction of regions contributing to the effect or the strength of the local electrostatic fields. However it may not be too grievous an error to consider N, α, b, Q, and η to be relatively constant, in which case the magnetic susceptibility would be linearly proportional to frequency; inspection of Fig. 4 shows this general result.

One reason to expect the measured magnetic moment to be small is that moments oriented along the electric field direction are perpendicular to the measuring magnetic field, and not detected. Therefore local, internal magnetic moments are expected to be larger than our measured values. The measured results appear to be consistent with the magnetic susceptibility values input as grain properties[2] to the effective medium theory[1,2] used to model measured permittivity spectra,[3,6] that is a relative magnetic susceptibility of a few tens. The correlation between permittivity and permeability spectra should not be too surprising, since an exact electromagnetic description of the μ and ϵ of composite material shows that the macroscopic permeability spectra are dependent upon grain permittivity, and vice versa.[2]

When the magnetic susceptibility of the ferroelectric samples was measured in a stripline cavity, a null value was obtained. However magnetic susceptibility measurements in a stripline cavity require the sample to be placed adjacent to the end wall of the cavity,[8] where the electric field is zero, and hence there would be no $E(t)$ based effect present.

It is possible that the measured magnetic aftereffect is due to the rotating charges, which result in local heating of the material to the Curie or melting temperature whereupon the effect ceases, allowing the material to cool in a minimum energy configuration where it is no longer subject to the effect. Alternatively, since relaxor ferroelectrics are known to depolarize with temperature,[10,11] it is possible that the local heating due to charge rotation acts to simply depolarize the region, which in turn eliminates the magnetic dipole moment.

CONCLUSIONS

Using a thin film permeameter[7] transient, high-frequency complex magnetic susceptibilities ranging from 0.1 to 2.5 have been measured in several nonpolarized and weakly polarized $BaTiO_3$, PZT, and carnauba wax samples. The motivation for such measurements comes from using an effective medium model for calculating the complex permittivity of granular materials[1,2] that is able to accurately model the measured complex permittivity spectra of ferroelectric material[3,6] if magnetic fields at the grain level are included in the model.

The origin of the magnetic susceptibility is thought to originate in the material with intense, local electrostatic fields created at domain discontinuities associated with grain boundaries. Large electrostatic energies can locally perturb the band diagram of anions in the atomic lattice, changing their response to an applied time varying electric field. An applied electric field acts to rotate an electric dipole moment, see Eq. (1), creating a magnetic quadrupole if the $\pm$ changes are balanced, and a net magnetic dipole that can be measured if imbalanced. The local magnetic field could be much larger than that measured by the permeameter, since the measurement is a volume averaged one, and the generated fields must be perpendicular to the plane of the pickup coil of the permeameter to be detected.

The measured magnetic susceptibilities are found to rapidly decrease while under measurement; for all samples the measured magnetic susceptibility disappeared after approximately 48 s. The magnetic response can be reintroduced into the sample a limited number of times, one to four, by placing the sample in a small 200 V/cm ac or dc polarizing field; after which the magnetic response is no longer seen in the sample. It is thought that the aftereffect has its origin in the moving charges that produce the magnetic field. Moving charges produce localized heating of the material; if the Curie temperature, melting point, or depolarization temperature[10] is exceeded locally, the effect ceases and the material cools into a new configuration that minimizes the electrostatic energy.

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